

1.131.989



PATENT SPECIFICATION

DRAWINGS ATTACHED

1.131.989

Date of Application and filing Complete Specification: 22 Dec., 1966.

No. 57394/66.

Application made in Netherlands (No. 6,516,902) on 24 Dec., 1965.

Complete Specification Published: 30 Oct., 1968.

© Crown Copyright 1968.

Index at acceptance:—B1 L5A; C5 E(D14, D17B)

Int. Cl.:—B 01 d 53/14

COMPLETE SPECIFICATION

Process for the Removal of Gas or Liquid Residues from Solvents used to treat Gases or Liquids

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the removal of gas or liquid residues from fat solvents (as defined below) which have been in contact with the said gas or liquid in a first zone.

In the present specification the term "gas" denotes both true gases and vapours. The gas for treatment with the solvent comprises one or more gaseous components such as hydrogen, carbon monoxide, light hydrocarbons, nitrogen, oxygen or water vapour, and one or more other compounds which are considered as impurities; for example, acid-reacting compounds such as hydrogen sulphide, sulphur dioxide, carbon dioxide and/or carbon oxysulphide. Possible gases for treatment are, for example, natural gas, air, gases obtained by partial or complete combustion of oil or coal, refinery gases, town gas, coke oven gas, water gas, propane and propylene. The liquid for treatment with the solvent comprises one or more liquid components such as hydrocarbons, and also contains one or more other compounds which are to be considered as impurities; for example, one or more of the above acid-reacting compounds. Mixtures of gas and liquid containing impurities may also be treated.

The impurities are not limited to those which are acid-reacting. Thus, the impurities may be alkaline-reacting compounds, such as ammonia or amines.

The process of the present invention is applicable to cases where impurities are removed with the aid of liquid solvents. With some solvents the removal is based on a

chemical reaction with the impurity; with other solvents the impurity is dissolved physically in the solvent. The use of solvents for dissolving acid-reacting compounds from gas or liquid is mostly based on the formation of salts of these compounds and/or a certain physical solubility.

Separation of the impurities is effected by intimately contacting the liquid solvent with the gas or liquid to be treated, by which contact the "fat solvent" is formed, i.e. the solvent laden ("fat") with impurities. The loading takes place in the first zone. It is usually effected in a column, the counterflow principle being preferably used. Normally, a vertical column is used, the treated gas or liquid leaving the column near or at the top while fat solvent (containing the absorbed impurities) leaves the column near or at the bottom. This column is mostly provided with fractionation trays, baffle plates or other contacting means. The term "absorption column" is used when a gas is contacted with the solvent and the term "extraction column" when a liquid is so contacted.

The fat solvent, however, also contains residues of the gas or liquid treated, for example, a portion of the hydrogen, carbon monoxide, nitrogen, oxygen and/or hydrocarbons originally present in the gas mixture. The fat solvent may contain these residues in the dissolved state or dispersed therein. The dispersed residues may still be gaseous and/or liquid.

In a known process for the removal of such gas or liquid residues the fat solvent is passed on from the lower part of the absorption or extraction column to an expansion vessel in which the pressure is reduced in order to remove practically all gas or liquid residues by volatilization (see "Gas Purification Processes" by G. Nonhebel, London, 1964, George Newnes Limited, page 264). The disadvantages of such a process are that an expansion vessel is required and that the

[Price 4s. 6d.]

resultant gas or liquid residues (which are entirely in the gaseous state after the expansion) still contain a small quantity of acid-reacting compounds. If hydrogen sulphide is present, the expanded gas is not suitable for many further applications, for example as fuel, without further treatment. In such cases a separate absorption column is necessary in order to absorb this small quantity of hydrogen sulphide from the expanded gas in a separate quantity of solvent.

It has now been found that a considerable simplification may be obtained by omitting the expansion vessel with separate absorption column and instead passing the fat solvent into a second zone in which, at a pressure lower than the pressure prevailing in the first zone, a second quantity of gas or liquid is in contact with solvent. In this way an integrated high/low pressure treatment of gas and liquid is achieved.

The first zone, therefore, has a pressure which is higher than that of the second zone. The gas residues dissolved and dispersed in the solvent in the first zone will, in the process according to the invention escape from the fat solvent and subsequently mix with the gas or liquid which is treated in the second zone. If the material treated in the first zone was a liquid, the liquid residues dispersed in the fat solvent will escape from the fat solvent only if these liquids go over into the gaseous state at the pressure prevailing in the second zone. It is also conceivable that the dispersed liquid residues in the second zone go partly over into the gaseous state.

The solvent introduced into the second zone which is laden with the impurities absorbed in the first zone will also release a small quantity of these impurities at the pressure prevailing in the second zone, which is lower than that in the first zone. However, this phenomenon is of little importance particularly in those cases in which the impurities are bound chemically.

According to the invention, therefore, a process for the removal of gas or liquid residues from a fat solvent (as defined above) which has been in contact in a first zone with the gas or liquid, comprises passing the fat solvent into a second zone which is at a pressure lower than the pressure prevailing in the first zone and in which a second quantity of gas or liquid is in contact with solvent.

Because the fat solvent containing gas or liquid residues is subjected in the second zone to a pressure which is lower than that in the first zone, these residues will mix in the gaseous state with the second quantity of gas or liquid which is in contact with the second quantity of solvent. For the absorption or extraction in the second zone, use may be made, as in the first zone, of a

column provided with fractionation trays, baffle plates or other contacting means. It is possible to pass the fat solvent used in the first zone into the bottom of such a column, i.e. below the contacting means, and to mix it with a further quantity of solvent. However, in this case the fat solvent does not come into contact with the contacting means present in the column. The fat solvent containing gas or liquid residues is therefore preferably passed to one or more of the fractionation trays, baffle plates or other contacting means of the absorption or extraction column.

In such a case the first and the second quantities of solvent together flow in a downward direction through the contacting means while the gas or liquid residues may go over into the gaseous state and be mixed with the second quantity of gas or liquid.

In the process according to the invention an expansion vessel with separate absorption column can therefore be omitted completely.

Thus, in the process according to the invention a mixture of fat solvents is eventually obtained, part of which has been in contact with gas or liquid in the first zone also, and part only in the second zone. In order to be able to re-use the fat solvent and/or to recover the absorbed impurities from the solvent (hydrogen sulphide, for example, being of particular importance as raw material for the production of sulphur), it is preferred to free the two quantities of solvent from absorbed impurities by regeneration after they have passed through the second zone. It is possible, after regeneration, to re-use a portion of the solvent for the contact in the first zone and another portion of the solvent for the contact in the second zone. Regeneration may be effected by fractional evaporation in a gas stripper, the pressure being considerably lower than that at which the impurities were absorbed in the solvent. The temperature is sufficiently high to allow the impurities present to evaporate from the fat solvent, the separated material leaving the gas stripper at or near the top. The fractional evaporation is generally carried out with the aid of steam, although it is also possible to use some other stripping medium, for example nitrogen.

As has already been stated above, hydrogen sulphide may be present as impurity in a gas or liquid to be treated. If the material to be treated also contains hydrocarbons, the fat solvent will also contain hydrocarbon residues in addition to hydrogen sulphide. In the regeneration of a fat solvent of this type a gas will therefore be formed which, in addition to hydrogen sulphide, will also have a certain hydrocarbon content. This is particularly disadvantageous if the hydrogen sulphide has to be used at a later stage for the preparation of elementary sulphur, since it is

known that in the Claus process for the preparation of sulphur by partial oxidation of hydrogen sulphide, very small quantities of hydrocarbons in the hydrogen sulphide to be burned are sufficient to give the sulphur produced an undesirable black colour. It is these hydrocarbons which exercise a very adverse effect on the colour of the sulphur produced. There is a particular risk of the residues being present in the fat solvent if this solvent is used for the extraction of liquids, since in that case the fat solvent contains dispersed residues of the extracted liquid, which represent considerably more material than the same volume of a dispersed gas.

Consequently, the process of the invention is preferably applied in those cases in which the fat solvent is laden with hydrogen sulphide and the gas or liquid residues comprise hydrocarbons. As a result of the pressure prevailing in the second zone which is lower than that in the first zone, the fat solvent will become less rich in hydrocarbon residues and consequently the hydrogen sulphide-containing gas released during the subsequent regeneration of the fat solvent is likewise less rich in hydrocarbons, as compared with the case in which the fat solvent is regenerated immediately after effluxing from the first zone. The hydrogen sulphide-containing gas freed by the regeneration is therefore preferably processed to elementary sulphur by means of partial oxidation with the aid of an oxygen-containing gas.

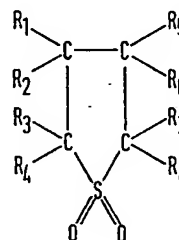
The pressure in the first zone is preferably between 7 and 70 kg/cm² since the pressures occurring most in practice are in this range. However, it is possible for the pressure in the first zone to be higher than 70 kg/cm². The pressure in the second zone is restricted in that it is lower than that in the first zone. Thus it is possible, for example, in the first zone to treat a liquid mixture of light hydrocarbons mainly consisting of propane and propylene with a solvent to remove the hydrogen sulphide, at a temperature lying between 30°C and 40°C and at a pressure which is between 20 and 25 kg/cm² abs. In addition, it is conceivable that in the second zone a gaseous mixture mainly consisting of methane and ethane is treated with solvent, likewise to remove hydrogen sulphide, at a temperature, lying between 30°C and 40°C, but at a pressure which is between 7 and 15 kg/cm². After the fat solvent has passed from the first zone into a second zone, hydrocarbon residues consisting mainly of propane and propylene will in such a case go over into the gaseous state and mix with light hydrocarbons which are treated in the second zone.

The temperatures at which the contact in the first zone and in the second zone take place are usually between 25°C and 135°C and preferably between 30°C and 80°C.

The solvent used may be any solvent which selectively dissolves the impurities. In order to dissolve acid-reacting impurities it is preferred to use an aqueous solution containing at least one amine which is weakly basic by nature and which reacts chemically with the acid-reacting compounds. Solutions of this type have the advantage that they can be easily regenerated. Examples of such amines are described in British patent specification No. 972,140. Particularly suitable is diisopropanolamine, since this amine is generally available in sufficient purity. This solvent is preferably used in an aqueous solution containing between 5% and 60% by weight of diisopropanolamine. In practice, commercial dipropanolamine mixtures are preferably used, such as those obtained as by-product in the preparation of diethanolamine. These commercial mixtures mostly consist of more than 90% by weight of diisopropanolamine and up to 10% by weight of mono- and tripropanol amines, and in addition may contain some diethanolamine.

Suitable amines for removing carbon dioxide and carbon oxysulphide are alkanol alkylamines and morpholines.

The process may also successfully be applied with the aid of solvents which physically dissolve acid-reacting compounds. In one embodiment the solvent contains at least one sulphone having the general formula:



in which at least 4 R's are hydrogen atoms and any remaining R's are alkyl groups each having 1 to 4 carbon atoms. Sulphones of this type are described in British patent specifications Nos. 997,169; 957,260 and 972,140. The preferred sulphone is cyclotetrahydro-methylene sulphone.

The use of sulphones of this type may result in the gases treated therewith containing a small amount of gaseous sulphone. Since this is undesirable for some applications it may in such cases be advisable to remove the sulphones completely or substantially completely from the gases treated, by contacting these gases with water or by absorbing the sulphones from the gases on an absorbent, for example on activated carbon.

In another embodiment the solvent contains an aliphatic acid amide. The use of such

acid amides is described in British patent specification No. 980,751. The most suitable acid amide is dimethyl formamide.

One of the problems that are met, in particular when treating gases in which the acid-reacting compounds have a high partial pressure, is the effective and complete removal of these compounds. Gases completely or substantially freed from acid-reacting compounds can be obtained after treatment with a solvent which, in addition to at least one amine having a weakly basic nature also contains a physical solvent. In this case, the acid reacting compounds are therefore partially dissolved physically and partially bound chemically. After the contact in the first zone, a certain quantity of the physically dissolved, acid-reacting gases will escape, in addition to the gas or liquid residues already mentioned, upon reducing the pressure on the fat solvent in the second zone, which gases will however be absorbed by the second quantity of solvent. A particular solvent comprising a combination of a physical and a chemical solvent, which is preferably used, contains 1 to 15% by weight of water, 15 to 35% by weight of di-isopropanolamine and 50 to 84% by weight of cyclotetrahydromethylene sulphone. In other instances, such a solvent may contain, for example, monoisopropanol amine, cyclotetrahydromethylene sulphone and water, or an alkanol alkylamine, cyclotetrahydromethylene sulphone and water. Suitable alkanol alkylamines are, for example, methylaminoethanol and ethylaminoethanol. Mixtures containing a morpholine, cyclotetrahydromethylene sulphone and water can also be used; suitable morpholines are morpholine itself and 2,6-dimethyl morpholine.

The process may also be used with solvents containing an N-alkylated pyrrolidone and/or an N-alkylated piperidone. Thus, a suitable solution may contain 30 to 60% by weight of diisopropanolamine and N-methyl pyrrolidone. A solution containing an alkanol alkylamine and/or a morpholine in addition to N-methyl pyrrolidone can also be used.

The invention may be performed in various ways, and a specific embodiment will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of a conventional process, given by way of comparison; and

Figure 2 is a schematic diagram of a process embodying the invention.

In the drawings auxiliary equipment, such as valves, pumps and control equipment are for the most part not shown.

In Figure 1, the conventional process for the removal of gas or liquid residues from fat solvents is shown. A feed is passed into the lower part of a column 2 via a line 1.

The feed may comprise gas, liquid or a

mixture of both, containing acid-reacting compounds as impurities. A solvent not rich in acid-reacting compounds is passed into the upper part of the column 2 via a line 3. The column 2 is the first zone referred to above. The solvent from the line 3 is in contact in this first zone with the gas or liquid from the line 1. Gas or liquid from which acid-reacting compounds have been wholly or partly removed leave the column 2 through a line 4, while the solvent rich in acid-reacting compounds, i.e. the fat solvent, leaves the column 2 through a line 5. In those cases in which gases are contacted with a solvent in the column 2, this column will be provided with fractionation trays, baffle plates or other contacting means and such a column may be termed an absorption column. If in the column 2 liquids or mixtures of gases and liquids are treated, the column may be provided with layers of packing units serving as contacting means. In such cases the column 2 may be termed an extraction column. The pressure in the column 2 is usually between 7 and 70 kg/cm² abs., since the pressures occurring in practice are usually in this range, but pressures above 70 kg/cm² or below 7 kg/cm² abs. may be applied.

As solvent, any solvent suitable for absorbing acid-reacting compounds may be used, for example, a solvent containing cyclotetrahydromethylene sulphone, one or more amines and water.

The solvent (fat) flowing through the line 5 laden with acid-reacting compounds contains gas or liquid residues originating from the feed flowing into the column 2 through the line 1. In the conventional process the fat solvent is passed into an expansion vessel 6 through the line 5, the pressure in this vessel being lower than that in the column 2, for example lying between 1.5 and 7 kg/cm² abs., as a result of which the gas or liquid residues are separated from the fat solvent substantially completely in the gaseous state. The gas thus formed in the expansion vessel 6 will also contain a small quantity of acid-reacting compounds which, in so far as hydrogen sulphide is concerned, will mostly have to be removed from this gas in order that the gas can be used elsewhere. To this end the gas leaves the expansion vessel 6 via a line 7 and subsequently flows into an absorption column 8 in which the gas is treated in counterflow with a solvent not rich in acid-reacting compounds which is introduced through a line 9 and leaves the column 8 through a line 10 as a solvent rich in acid-reacting compounds. The gas thus treated leaves the column 8 through a line 11.

The fat solvent containing the absorbed acid-reacting compounds leaves the expansion vessel 6 at the bottom via a line 12 and flows at a slightly further reduced pressure to a stripping column 13 which is heated by

means of a reboiler 14. The acid-reacting compounds which are driven out by heating leave the column 13 through a line 15. The solvent, no less rich in acid-reacting compounds, leaves the column 13 through a line 16 and flows through at least one heat exchanger 17, in which heat is exchanged with solvent rich in acid-reacting compounds flowing through the line 12, the cooled solvent subsequently flowing partly through the line 9, to the absorption column 8, partly through the line 3 to the column 2 and partly to a column 18. It is also possible to heat the fat solvent flowing through the line 12 by indirect heat exchange with steam or by using already available hot gases which must in any case be cooled, such as hot mixtures containing carbon dioxide, hydrogen and steam and which may have been formed from mixtures containing carbon monoxide and water, so that the fat solvent is then also heated by making use of the condensation heat of water. A feed which may consist of gas or liquid or of a mixture of the two flows into the column 18 through a line 19 and is treated in counter-flow at a pressure lower than that in the first zone with the solvent not rich in acid-reacting compounds from the line 16. The column 18 is the second zone referred to above. Gas or liquid from which acid-reacting compounds have been wholly or partly removed leaves the column 18 through a line 20. Fat solvent laden with acid-reacting compounds leaves the column 18 through a line 21 and is subsequently combined with the fat solvent flowing through the line 12.

Figure 2 shows a process according to the present invention. In this Figure, the items designated by the same numerals as in Figure 1 have the same function as the corresponding items of Figure 1. In the present case, the expansion vessel 6, the absorption column 8 and the lines 7, 9, 10 and 11 of Figure 1 are not present and according to the process of the present invention the fat solvent used in the column 2 is passed through the line 5 to the column 18 which is at a pressure lower than that in the column 2 and in which acid-reacting compounds are removed from gas or liquid flowing through the line 19. As a result of the pressure prevailing in the column 18, which pressure is lower than that in the column 2, the gas or liquid residues which are present in the fat solvent flowing through the line 5 are therefore entrained by the gas or liquid treated in the column 18. In the case shown, mixing of the fat solvent flowing through the line 5 and containing gas or liquid residues is carried out on one of the fractionation trays present in the absorption column 18, although this mixing operation could be carried out at the bottom of the absorption column 18.

The invention will now be further elucidated with reference to the following Example.

EXAMPLE

A liquid having a temperature of 40°C is introduced into the bottom of an extraction column. The composition of the liquid is as follows:—

Component	% by weight	
H ₂ S	0.0843	
CH ₄	0.3	
C ₂ H ₆	7.8	75
C ₃ H ₈	26.0	
Butanes	64.8	
Pentanes	1.0	

The pressure prevailing in the extraction column is 28 kg/cm² abs.; as contacting means use is made of Raschig rings.

An aqueous liquid containing diisopropanolamine is introduced into the top of the extraction column. This solution flows down past the Raschig rings, extracting hydrogen sulphide from the hydrocarbons flowing upwards. The solvent laden with hydrogen sulphide and contaminated with 0.05 to 0.10% by weight of dissolved and dispersed hydrocarbons leaves the extraction column at the bottom, then passes a control valve for the level of the liquid in the extraction column and is subsequently passed onto the fifth tray from the bottom of an absorption column. A gas to be freed from hydrogen sulphide is passed to the bottom of the absorption column at a temperature of 40°C, the gas having the following composition:

Component	% by weight	
H ₂	7.9	100
H ₂ S	5.4	
CH ₄	16.1	
C ₂ H ₆	19.1	
C ₃ H ₈	22.2	
Butanes	20.6	105
Pentanes	4.9	
Hexanes	3.4	
H ₂ O	0.4	

An aqueous solution containing diisopropanolamine is introduced into the top of the absorption column, which solution while flowing downwards absorbs hydrogen sulphide from the gas flowing upwards. The pressure in the absorption column is 5.0 kg/cm² abs., so that dissolved and dispersed impurities in the fat solvent from the extraction column change into the gaseous state and mix with the gas flowing upwards in the absorption column. This change into the gaseous state takes place thus on the lower five trays of the absorption column. After the fat solvent has passed into the absorption column it mixes with the absorption liquid already pre-

sent in the column, both solvents flowing downwards together and subsequently leaving the absorption column in the mixed state. The two solvents are then regenerated together in a column provided with trays at a temperature at the bottom of the column of 113°C and a pressure of 1.45 kg/cm² abs., the regenerated solvent being subsequently recycled partly to the extraction column and partly to the absorption column.

- 10 If in the Example the fat extraction liquid from the extraction column, which liquid is contaminated with hydrocarbons, were not passed to the absorption column but were to be passed directly to the regeneration column, an expansion vessel with matching absorption column would have to be arranged between the extraction column and the regeneration column in order to prevent the hydrogen sulphide-containing gas leaving the regeneration column from being contaminated with hydrocarbons.

WHAT WE CLAIM IS:—

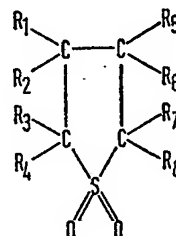
1. A process for the removal of gas or liquid residues from fat solvents (as hereinbefore defined) which have been in contact in a first zone with the gas or liquid, which comprises passing the fat solvent into a second zone which is at a pressure lower than the pressure prevailing in the first zone and in which a second quantity of gas or liquid is in contact with solvent.
2. A process as claimed in Claim 1 in which the second zone is an absorption or extraction column to one or more of the fractionation trays, baffle plates or other contacting means of which column the fat solvent containing gas or liquid residues is passed.
3. A process as claimed in Claim 1 or Claim 2 in which after having passed through the second zone the solvent is freed from absorbed impurities by regeneration.
4. A process as claimed in any of the preceding claims in which the fat solvent is laden with hydrogen sulphide and the gas or liquid residues comprise hydrocarbons.
5. A process as claimed in Claim 4 in which the gas freed by regeneration and containing hydrogen sulphide is processed to elementary sulphur by partial oxidation with the aid of an oxygen-containing gas.
6. A process as claimed in any of the preceding claims in which the fat solvent comes from a first zone in which the pressure is between 7 and 70 kg/cm².
7. A process as claimed in any of the preceding claims in which the solvent is an aqueous solution containing at least one amine which is weakly basic by nature.

8. A process as claimed in Claim 7 in which the solvent is an aqueous solution containing between 5% and 60% by weight of diisopropanolamine.

9. A process as claimed in Claim 7 in which the solvent contains an alkanol alkylamine.

10. A process as claimed in Claim 7 in which the solvent contains a morpholine.

11. A process as claimed in any of the preceding claims in which the solvent contains at least one sulphone having the general formula:



- in which at least four R's are hydrogen atoms and any remaining R's are alkyl groups each having 1 to 4 carbon atoms.

12. A process as claimed in Claim 11 in which the solvent contains cyclotetrahydromethylene sulphone.

13. A process as claimed in any of the preceding claims in which the solvent contains an aliphatic acid amide.

14. A process as claimed in Claim 12 in which the solvent comprises 1 to 15% by weight of water, 15 to 35% by weight of diisopropanolamine and 50 to 84% by weight of cyclotetrahydromethylene sulphone.

15. A process as claimed in any of Claims 1 to 13, in which the solvent contains an N-alkylated pyrrolidone and/or an N-alkylated piperidone.

16. A process as claimed in Claim 1 and substantially as described.

17. A process for the removal of gas or liquid residues from fat solvents (as hereinbefore defined), substantially as described with reference to Figure 2 of the accompanying drawing.

18. A process for the removal of gas or liquid residues from fat solvents (as hereinbefore defined), substantially as described in the Example.

19. Fat solvents (as hereinbefore defined) which have been freed from gas or liquid residues by a process as claimed in any of the preceding claims.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

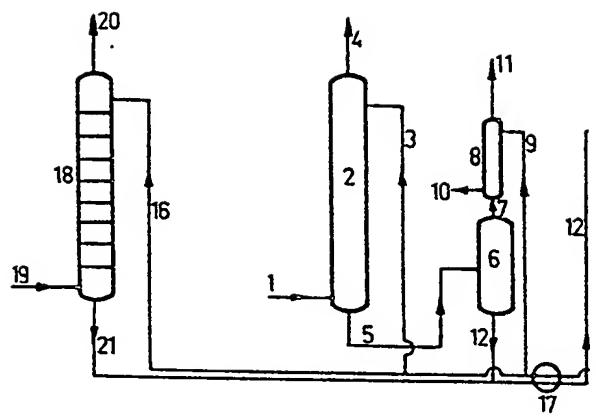


FIG.1

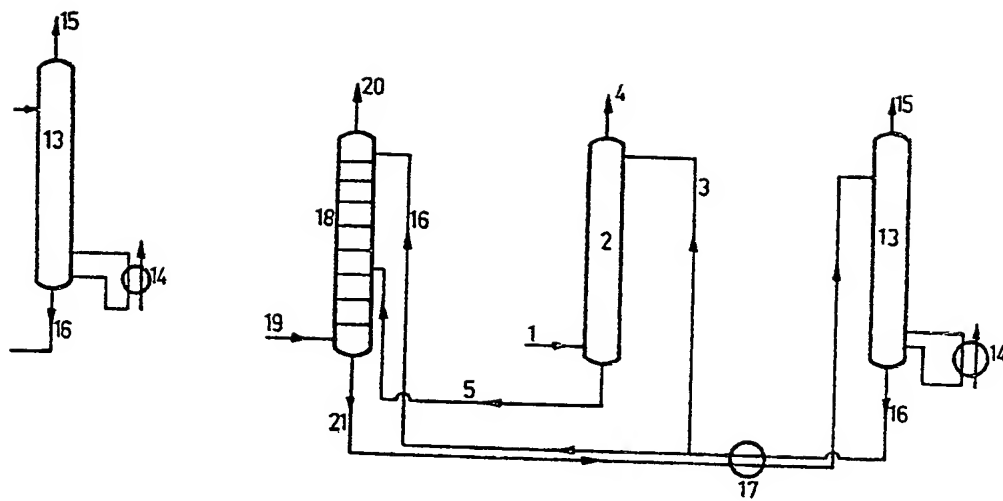


FIG.2

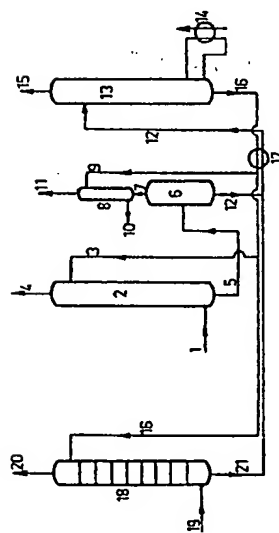


FIG. 1

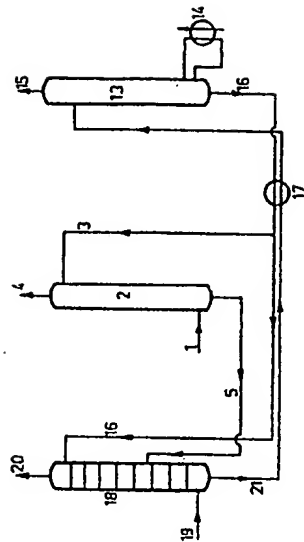


FIG. 2

THIS PAGE BLANK (USPTO)